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REPORT OF STUDY OF MAJOR INDUSTRIAL WASTES FROM THE PETROCHEMICAL INDUSTRIES

Rolf Eliassen Associates, Incorporated
Winchester, Massachusetts

September 1957

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REPORT OF STUDY
OF
MAJOR INDUSTRIAL WASTES
FROM THE
PETROCHEMICAL INDUSTRIES

FOR THE

ROBERT A. TAFT SANITARY ENGINEERING CENTER

PUBLIC HEALTH SERVICE

CINCINNATI, OHIO

BY

ROLF ELIASSEN ASSOCIATES, INC.

WINCHESTER, MASS.

SEPTEMBER 1957

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ROLF ELIASSEN ASSOCIATES, INC.

15 HILLSIDE AVENUE · WINCHESTER, MASSACHUSETTS

RESEARCH / DEVELOPMENT / TESTING / CONSULTATION

September 20, 1957

Mr. Bernard B. Berger, Chief
Water Supply and Water Pollution Program
Robert A. Taft Sanitary Engineering Center
U.S. Public Health Service
4676 Columbia Parkway
Cincinnati 26, Ohio

Dear Mr. Berger:

As requested by your office we have proceeded on a study of the major industrial wastes which might be expected in the chemical industries dependent on coal and petroleum as the source of raw materials and intermediates. We have established criteria for selecting chemicals for special studies on the basis of tonnages produced as tabulated in the latest production figures.

The procedure followed in this study was to scrutinize the major basic raw materials produced from petroleum, natural gas and coal. Primary end products and the probable constituents in the wastes were then listed to indicate major fields of study for your group. From the tabulation of the major producers of these raw chemicals and intermediates you will note that the potentials of stream pollution are national in scope. A research program concentrating on these industries is most assuredly in order because their phenomenal growth includes so many chemicals which have not been studied from the standpoint of waste treatment by chemical, physical and biological processes. It is our hope that this report will serve as the basis for a conference on the course of action which your group should follow in tackling this problem. In our estimation it has one of the highest pollution potentials of any group of industries now threatening the water resources of the nation.

This study has been carried out by my associate, Dr. James M. Symons, with advice and counsel from Dr. Ross E. McKinney and the writer. We appreciate the cooperation which you have given us personally in delineating this vast problem and the ideas contributed by Mr. Gerald N. McDermott of your staff. Dr. Symons and I look forward to meeting with you in the near future to discuss the report in detail in relation to the research program which you will inaugurate within your group.

Respectfully submitted,

ROLF ELIASSEN ASSOCIATES, INC.

Rolf Eliassen

Rolf Eliassen
President

STATEMENT OF THE PROBLEM

As the industrial economy of the United States expands so does the problem of the disposal of the wastes from these industries. The demand for water, both for industrial and municipal uses, is also increasing, making the need for treatment of industrial wastes before their eventual discharge into watercourses ever more imperative. Many of the industrial wastes are amenable to treatment by one or more of the common unit operations employed by sanitary engineers in the design of waste treatment plants. Design criteria for the processing of many industrial wastes have been developed by the Public Health Service, state and interstate health agencies, consultants and the industries themselves. These include the textile, food processing, distilling, paper, metallurgical, metal plating and many other industries which have been established for many years.

The organic chemical industries using petroleum, natural gas and coal as raw materials have grown in a phenomenal manner in the past decade. Many new products are being created each year by polymer chemists. Waste treatment processing has not kept up with the growth of this industry, with the result that many pollutional problems have been created.

Public health departments of many states are not equipped to render the specialized assistance requested by industries and their consultants for the solution of these new problems. The Robert A. Taft Sanitary Engineering Center of the Public Health Service is directed by law to assist states in the solution of vexing problems in stream pollution control. But is is impossible to solve all of the problems of such a complex industry. The logical approach for the Public Health Service would be to carry out research on the treatment

of selected categories of the most prevalent wastes from the organic chemical industry and to prepare an Industrial Wastes Guide for the industry. This Guide can specify the manner in which specific industrial waste surveys can be carried out, the manner in which pilot plant studies can be conducted to determine design criteria for the most economical treatment plants, and other factors which will assist the industry to comply with the requirements of stream pollution control agencies.

An extensive research program must be carried out by the Robert A. Taft Sanitary Engineering Center in order to obtain the information necessary to prepare such a Guide. This program must be directed toward a solution of the most pressing problems of the greater segment of the industry, which in turn would indicate solutions to the treatment problems created by those chemicals which are most widely used.

This study has been carried out in an attempt to determine from published data the extent of production of the major organic chemicals - from raw materials to end products - and to delineate the wastes associated with this production. The material contained in this report can then be used to indicate the substances which should be studied in a waste treatment research program designed to assist states and industries in solving their water pollution problems.

OBJECTIVES OF THE STUDY

The study which forms the basis for this report had the following objectives:

1. To survey the literature of industrial chemistry and chemical economics to determine the latest available data on the production of synthetic organic chemicals derived from petroleum, natural gas and coal.
2. To select the major crude products which are likely to occur in the greatest quantities in the wastes from the above organic chemical industries.
3. To select the "intermediate" organic chemicals which are most prevalent in the manufacture of organic end products, and therefore most likely to occur in liquid industrial wastes.
4. To determine the companies which utilize the major crude products and produce the "intermediates" and to list their locations to show the national occurrence of the problem.
5. To present the flow patterns of use of the major selected chemicals in the production of end products from the crudes and intermediates.
6. To study manufacturing processes for the end products and relate these to the production of liquid industrial wastes.
7. To recommend a course for research in the field of treatment of synthetic organic chemical wastes, based on a national need for research on the part of industries, states and interstate control agencies.

APPROACH TO THE PROBLEM

The entire organic chemical industry is very complex. Starting with natural gas, petroleum, coal, wood, sugars, fats, oils, starches, protein materials, cotton linters, pentosaniferous materials, milk, coffee, and seaweed, all the myriad of organic chemicals produced today are synthesized. These chemicals fall into four natural categories:

1. Basic Raw Materials
2. Key Intermediates
3. Minor Intermediates
4. End Products

For example, in the production of the synthetic fiber "Perlon", the basic raw material is benzene, the intermediates are cyclohexane, cyclohexanoxime, and caprolactam, and the end product is "Perlon". In this case, cyclohexane is a key intermediate, also being used in the manufacture of other products. For example, cyclohexane can be converted to adipic acid, thence to adiponitrile, and finally to hexamethylenediamene which is used in the manufacture of "Nylon". Therefore, cyclohexane would probably appear in the waste streams from the production of both "Perlon" and "Nylon".

Cyclohexanoxime and caprolactam, on the other hand, are defined as minor intermediates since they would only appear in the waste stream from the manufacture of "Perlon". Unfortunately, these categories are not exactly defined, but they form a technical basis upon which this study may proceed.

The United States Tariff Commission lists production figures for "Crude Products Derived from Petroleum or Natural Gas" and "Intermediates". Both lists are fairly long, especially the intermediate

list due to the complexity of the organic chemical industry. However, for this study both lists will be shortened to the most prevalent chemicals in each category. These will cover the bulk of the total production of basic and key intermediate chemicals in this country.

Once selected, the utilization of these major chemicals is then traced through all of the minor intermediates to the final end products. At this stage the over-all picture begins to pyramid since the final organic end products produced in this country today number in the thousands. Simplifying steps can be taken, however, to cover a major portion of the field without examining all of the problems. Several end products are manufactured to a greater extent than others; several are manufactured by a number of different processes. In either case, study of these is justified on the basis of frequency and quantity of occurrence in industrial processes and hence in wastes.

In summary, this report takes the following form:

1. Fifteen major chemicals to be studied.
2. Chemical structure of the major chemicals to be studied.
3. What companies make these major chemicals and the locations of their plants.
4. Flow patterns of use for the fifteen major chemicals.
5. Selection of fifteen end product categories for study.
6. Flow patterns of production of end products in categories selected and probable constituents of waste streams,
7. Manufacturing processes for end products in categories selected where available.

SELECTION OF MAJOR CHEMICALS FOR STUDY

The United States Tariff Commission Bulletin "Synthetic Organic Chemicals, United States Production 1954" lists, in the category defined as "Crude Products Derived from Petroleum and Natural Gas", seventeen specific chemicals with a total production in 1954 of 13,446 million pounds, a 20.6 per cent increase over the 1953 production. These are the latest complete production figures published. Of these seventeen chemicals, eight were selected for study. These eight represented 68.9 per cent of the total production. Each chemical chosen was produced in excess of 600 million pounds and represented at least 4.5 per cent of the total production of the petrochemical industry.

The eight chemicals selected are as follows:

CHEMICAL	ANNUAL PRODUCTION IN MILLION POUNDS
Benzene	673
1,3 Butadiene	808
n-Butane	941
Ethylene	2,344
Propane	1,675
Propylene	1,203
Toluene	890
Xylene	726
Total	9,260

In the category defined as "Cyclic Intermediates" a total of 225 chemicals were listed, their total 1954 production being 4,614 million pounds. Of this total only 83 per cent or 3,831 million pounds were listed, due to incomplete reports from the 142 companies which manufactured these chemicals. Of the 225 chemicals listed, twenty-five were produced in excess of 0.1 per cent of the total market.

These twenty-five chemicals are as follows:

CHEMICAL	ANNUAL PRODUCTION IN THOUSAND POUNDS
2 Amino - 1 Naphthalensulfonic Acid	3,825
Aniline	97,349
o-Benzoylbenzoic Acid	5,180
Monochlorobenzene	367,947
1 Chloro - 2,4 Dinitrobenzene	4,150
alpha Chlorotoluene	11,545
Cresol	22,036
Cresylic Acid	26,635
Cumene	33,118
Cyclohexane	217,619
o-Dichlorobenzene	23,890
p-Dichlorobenzene	51,871
2,4 Dichlorobenzene	17,215
N,N Dimethylaniline	7,017
Dodecylbenzene (includes keryl types)	357,781
Ethylbenzene	825,010
Naphthalene	71,151
Nonylphenol	9,196
Phenol	369,673
Phthalic Anhydride	253,847
Styrene	703,169
Salicylic Acid	15,053
1,2,4,5 Tetrachlorobenzene	5,122
p-Xylene	59,188
Total	3,558,587

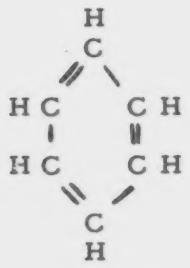
Of these twenty-five chemicals, seven were selected for study, representing 82.0 per cent of the total production. Each chemical selected was produced in excess of 200 million pounds and represented 5.2 per cent of the total production or more.

The seven chemicals selected are as follows:

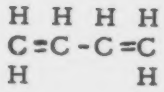
CHEMICAL	ANNUAL PRODUCTION IN MILLION POUNDS
Monochlorobenzene	368
Cyclohexane	218
Dodecylbenzene	358
Ethylbenzene	825
Phenol	417
Phthalic Anhydride	254
Styrene	703
Total	3,143

These and the eight crude products on page 6 are the fifteen major chemicals which represent the bulk of the basic organic chemical raw materials produced in this country to supply the chemical processing industries. These basic organic chemical raw materials are themselves produced from petroleum, coal, and natural gas.

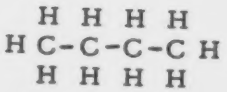
CHEMICAL STRUCTURE OF SELECTED CHEMICALS



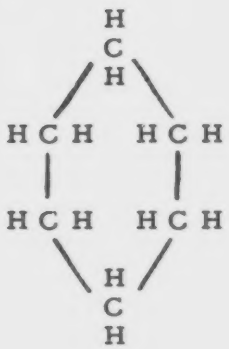
BENZENE



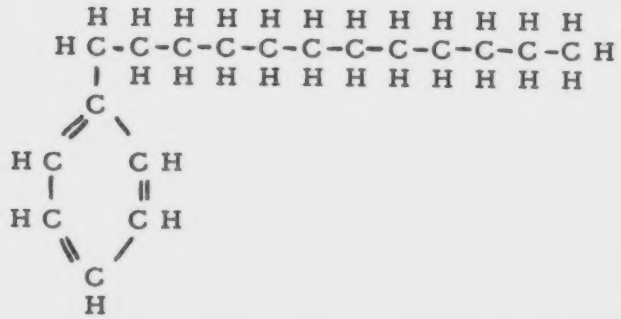
1, 3 BUTADIENE



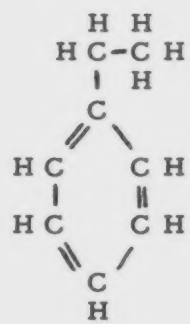
n-BUTANE



CYCLOHEXANE

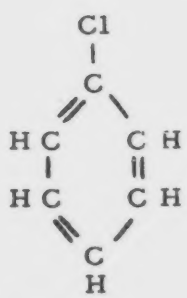


DODECYLBENZENE

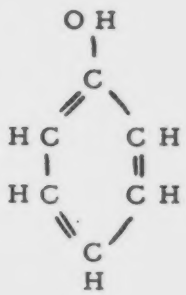


ETHYLBENZENE

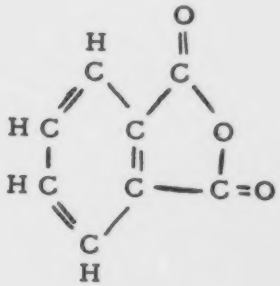
ETHYLENE



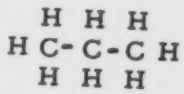
MONOCHLOROBENZENE



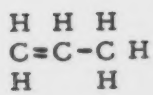
PHENOL



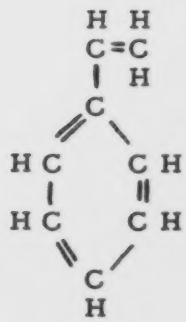
PHTHALIC ANHYDRIDE



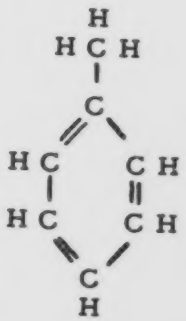
PROPANE



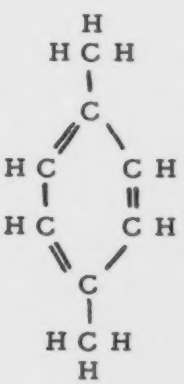
PROPYLENE



STYRENE



TOLUENE



p-XYLENE

COMPANIES PRODUCING MAJOR SELECTED CHEMICALS

Data from the United States Tariff Commission Bulletin "Synthetic Organic Chemicals, United States Production, 1954" was used to compile this list of companies which are presented in the order of number of chemicals produced.

Dow Chemical Company

- Benzene
- 1, 3 Butadiene
- Monochlorobenzene
- Ethylbenzene
- Ethylene
- Propylene
- Toluene
- Styrene

Allied Chemical and Dye Corp. (Barrett Div.)

- Cyclohexane
- Ethylbenzene
- Phthalic Anhydride

Allied Chemical and Dye Corp. (Solvay Process Div.)

- Monochlorobenzene

Allied Chemical and Dye Corp. (National Aniline Div.)

- Dodecylbenzene
- Phthalic Anhydride
- Styrene

Allied Chemical and Dye Corp. (Semet-Solvay Div.)

- Propylene

Dow Chemical Co. (Styrene Div.)

- Benzene
- Ethylbenzene
- Ethylene
- Propylene

Dow Chemical Co. (Styrene Div.)(Continued)

Styrene
Toluene
Xylene

Monsanto Chemical Company

Monochlorobenzene
Dodecylbenzene
Ethylbenzene
Ethylene
Phthalic Anhydride
Styrene
Toluene

Union Carbide and Carbon Co. (Carbide and Carbon Chemicals Co.)

Benzene
1, 3 Butadiene
Ethylbenzene
Ethylene
Propane
Propylene
Toluene

Standard Oil Company of Indiana

Benzene
Dodecylbenzene
Ethylene
Propane
Propylene
Toluene
Xylene

Shell Oil Company

Benzene
Cyclohexane
Propane
Propylene
Toluene
Xylene

Standard Oil Company of California

Benzene
n-Butane
Dodecylbenzene
Phthalic Anhydride
Toluene
Xylene

Humble Oil and Refining Company

1, 3 Butadiene
Cyclohexane
Ethylbenzene
Toluene
Xylene

Esso Standard Oil Co. (Louisiana Div.)

Benzene
1, 3 Butadiene
Ethylene
Propane
Propylene

Continental Oil Company

n-Butane
Dodecylbenzene
Propane
Toluene
Xylene

E. I. duPont de Nemours and Company, Inc.

Monochlorobenzene
Cyclohexane
Ethylene
Propylene

Pan American Refining Company

Benzene
Propane

Pan American Refining Company (Continued)

Toluene

Xylene

Pure Oil Company

n-Butane

Propane

Toluene

Xylene

Shell Chemical Company

Benzene

1, 3 Butadiene

Ethylene

Propane

Note: Only companies producing four or more of the major chemicals are listed.

LOCATION OF PLANTS PRODUCING THESE CHEMICALS

The locations of the plants producing these chemicals are taken from the same United States Tariff Commission Bulletin mentioned previously and are listed in the same order as in the previous section.

Dow Chemical Company

Pittsburg and Torrance, Calif., Gales Ferry, Conn., Freeport, Texas

Allied Chemical and Dye Corp. (Barrett Div.)

Calumet City and Chicago, Ill., Detroit, Mich., Edgewater, N. J., Greensboro, N. C., Ironton, Toledo and Youngstown, Ohio, Bethlehem and Philadelphia, Pa.

Allied Chemical and Dye Corp. (Solvay Process Div.)

Solvay Village, N. Y.

Allied Chemical and Dye Corp. (National Aniline Div.)

Buffalo, N. Y., Hopewell, Va., Moundsville, W. Va.

Allied Chemical and Dye Corp. (Semet-Solvay Div.)

Tonawanda, N. Y.

Dow Chemical Co. (Styrene Div.)

Los Angeles, Calif.

Monsanto Chemical Company

Anniston, Ala., Long Beach and Santa Clara, Calif., Monsanto, Ill., Camden, N. J., Everett and Springfield, Mass., Trenton, Mich., Texas City, Texas, Nitro, W. Va.

Union Carbide and Carbon Co. (Carbide and Carbon Chemicals Co.)

Whiting, Ind., Niagara Falls, N. Y., Port Lavaca and Texas City, Texas, S. Charleston, W. Va.

Standard Oil Company of Indiana

Wood River, Ill., Whiting, Ind., Sugar Creek, Mo.

Shell Oil Company

Martinez and Wilmington, Calif., Roxana, Ill., Norco, La., Deer Park, Texas

Standard Oil Company of California

Bakerfield, El Segundo and Richmond, Calif.

Humble Oil and Refining Company

Baytown, Texas

Esso Standard Oil Co. (Louisiana Div.)

Baton Rouge, La.

Continental Oil Company

Ponca City, Okla.

E. I. duPont de Nemours and Company, Inc.

Newport and Wilmington, Del., Chicago, Ill., E. Chicago, Ind., Ft. Madison, Iowa, Louisville, Ky., Everett, Mass., Flint, Mich., Carney's Point, Grasselli, Linden, Newark, New Brunswick, Parlin and Perth Amboy, N. J., Niagara Falls, N. Y., Cleveland, Ohio, Philadelphia, Pa., Chattanooga, Tenn., La Porte and Orange, Texas, Martinville, Va., Belle, W. Va.

Pan American Refining Company

Texas City, Texas

Pure Oil Company

Toledo, Ohio, Dollarhide, Snyder, Nederland and Van, Texas, Cabin Creek, W. Va., Worland, Wyo.

Shell Chemical Company

Martinez, Los Angeles and Pittsburg, Calif., Deer Park, Texas

FLOW PATTERNS OF USE FOR MAJOR SELECTED CHEMICALS

Flow patterns of use are presented from data contained in Stanford Research Institute "Chemical Economics Handbook", Volume VI, Organic Chemicals, for the major selected chemicals in the following alphabetical order:

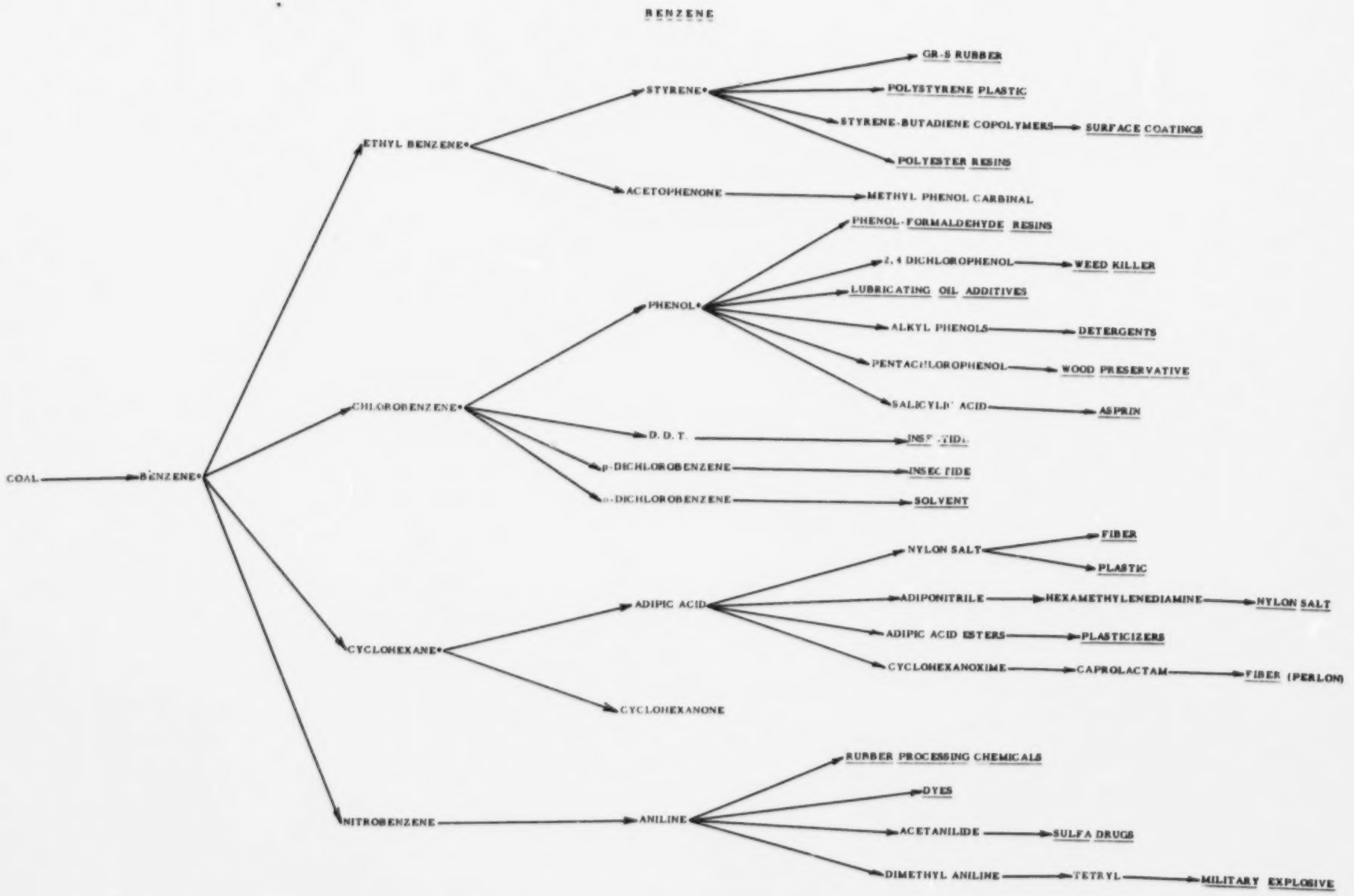
Benzene	Phenol
1,3 Butadiene	Phthalic Anhydride
n-Butane	Propane
Monochlorobenzene	Propylene
Cyclohexane	Styrene
Dodecylbenzene	Toluene
Ethylbenzene	Xylene
Ethylene	

On each of the charts which follow, any of the fifteen major chemicals which are included are noted with an asterisk (*) and all of the end products are underlined.

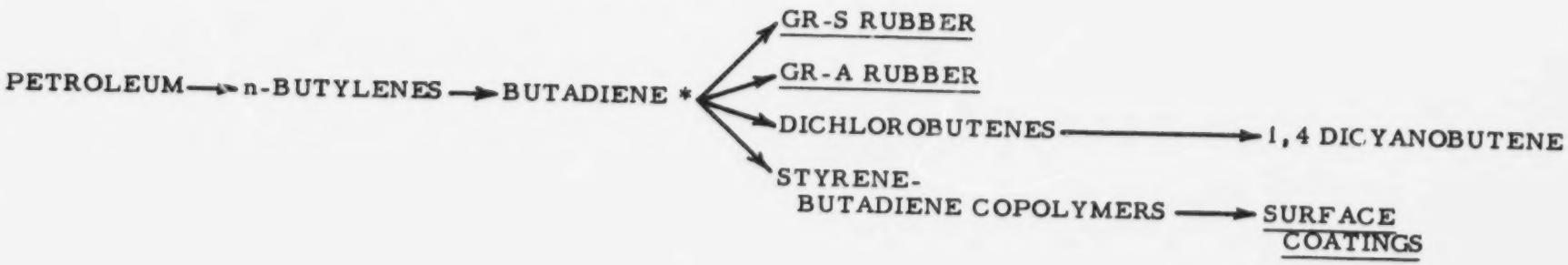
These charts are rather complete but several factors related to the method used to construct them must be clearly understood in order to avoid misinterpretation. These are as follows:

1. Only chemicals which were produced in quantities in excess of twenty-five million pounds and/or had a production value of over five million dollars in 1953 are shown.
2. If a chemical was produced in excess of twenty-five million pounds, but did not have a production value of five million dollars, it is shown.
3. The product flow is based entirely on the flow of carbon atoms involved.

4. Only intermediates which have sufficient economic significance of their own, or which are necessary for a clear understanding of the product flow, are shown. All intermediates not meeting these criteria are omitted; e.g. in going from adol to n-butyl alcohol, the intermediate crotonaldehyde is omitted. Intermediates are always shown when there is a change in the number of carbon atoms; e.g. acetaldehyde to adol.
5. In order to simplify the charts it has been assumed that petroleum not natural gas was the principal source of ethylene and propylene in 1953. Actually, the sources of these two olefins were approximately half petroleum and half natural gas.
6. The product flow is continued only after one principal source. For example, although ethylene and propylene are also made from propane refined from natural gas, the product sequence has been shown after petroleum as their principal source. A similar chart could have been drawn from natural gas.
7. When a chemical is made from two or more intermediates the product flow is continued only after the intermediate supplying the greatest number of carbon atoms. In one extreme case, vitamin B_1 is made from seven intermediates, but it is shown only after ethyl acetoacetate which supplies three of the twelve carbon atoms in the final molecule.
8. Some military products were included because of their importance in national defense programs.


BENZENE
COAL
BENZENE
ETHYL BENZENE
STYRENE
GR-S RUBBER
POLYSTYRENE PLASTIC
STYRENE-BUTADIENE COPOLYMERS
SURFACE COATINGS
POLYESTER RESINS
ACETOPHENONE
METHYL PHENOL CARBINAL
CHLOROBENZENE
PHENOL
PHENOL-FORMALDEHYDE RESINS
2, 4 DICHLOROPHENOL
WEED KILLER
LUBRICATING OIL ADDITIVES
ALKYL PHENOLS
DETERGENTS
PENTACHLOROPHENOL
WOOD PRESERVATIVE
SALICYLIC ACID
ASPRIN
D. D. T.
INSECTICIDE
p-DICHLOROBENZENE
INSECTICIDE
o-DICHLOROBENZENE
SOLVENT
CYCLOHEXANE
ADIPIC ACID
NYLON SALT
FIBER
PLASTIC
ADIPONITRILE
HEXAMETHYLENEDIAMINE
NYLON SALT
ADIPIC ACID ESTERS
PLASTICIZERS
CYCLOHEXANOXIME
CAPROLACTAM
FIBER (PERLON)
CYCLOHEXANONE
NITROBENZENE
ANILINE
RUBBER PROCESSING CHEMICALS
DYES
ACETANILIDE
SULFA DRUGS
DIMETHYL ANILINE
TETRYL
MILITARY EXPLOSIVE

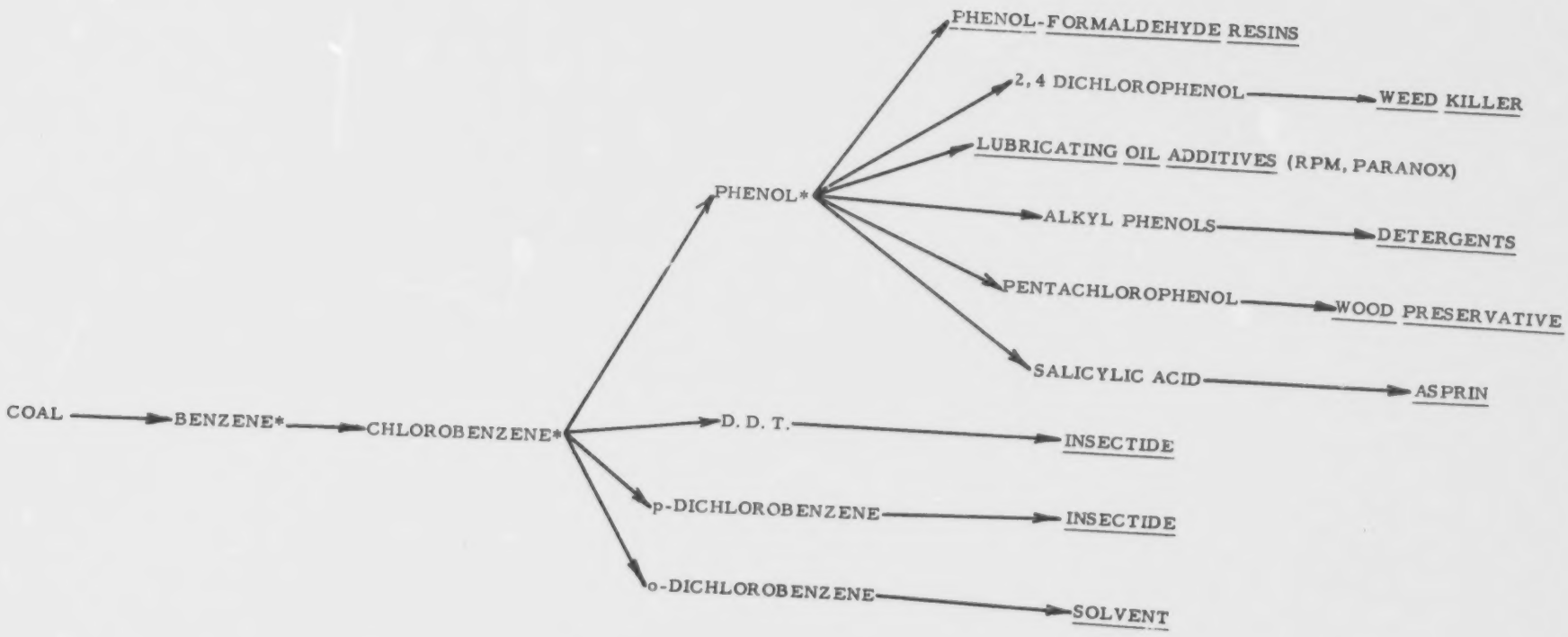
1,3 BUTADIENE

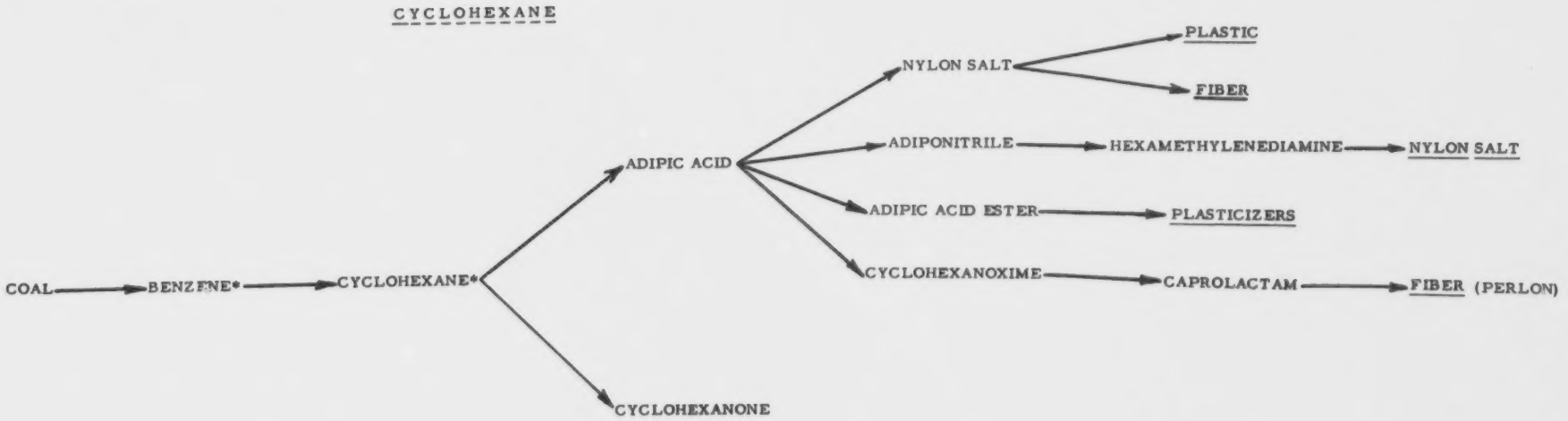


n-BUTANE

NATURAL GAS ⟶ BUTANE *

MONOCHLOROBENZENE

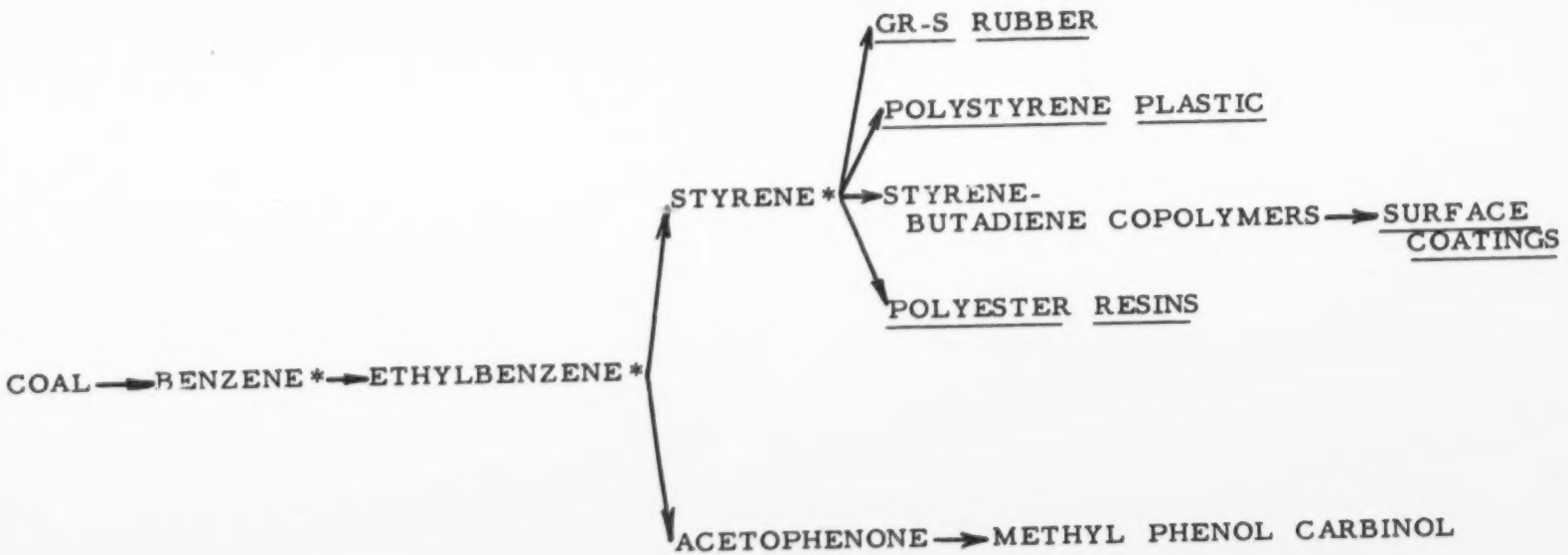


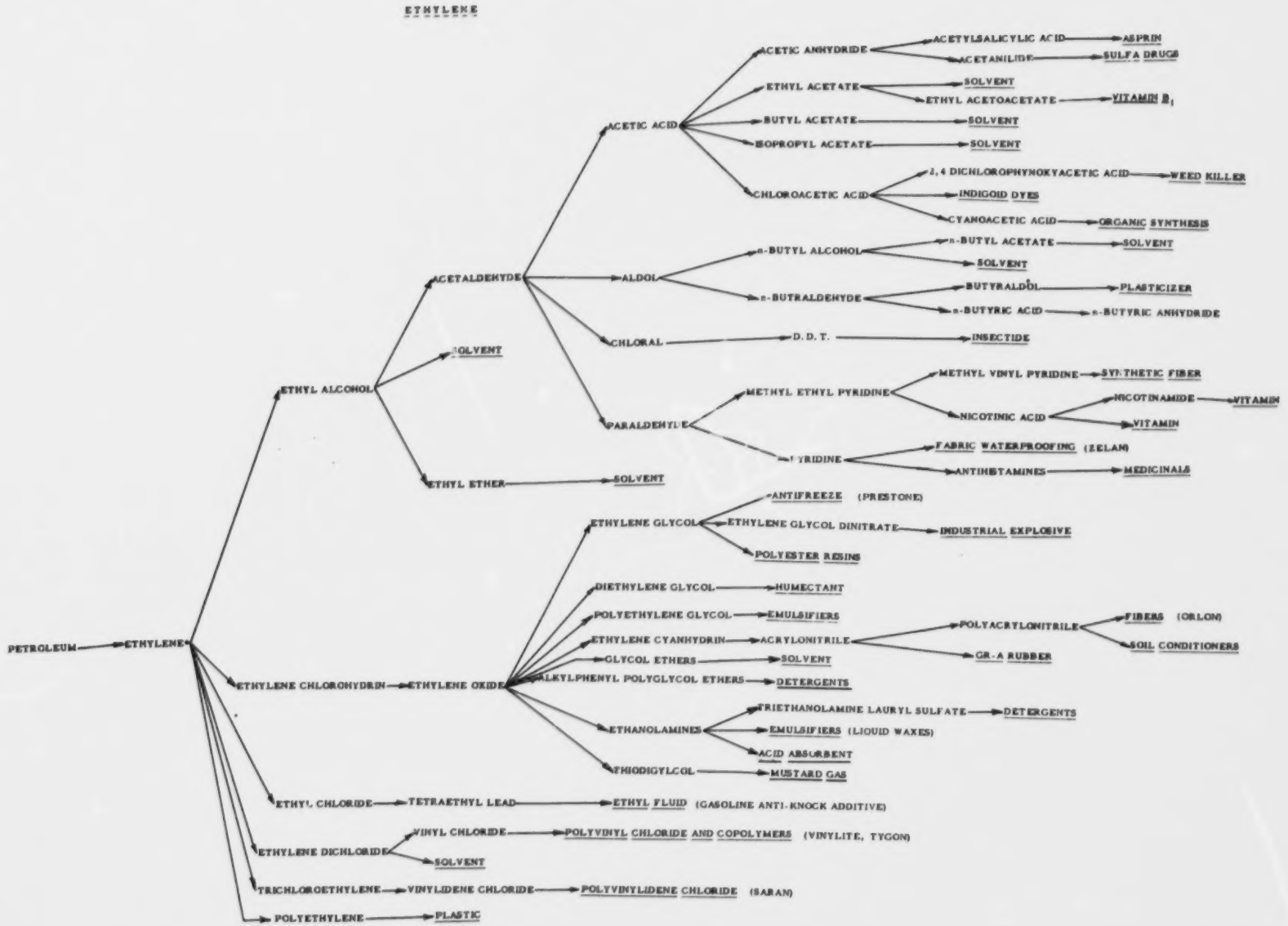

CYCLOHEXANE
COAL
BENZENE*
CYCLOHEXANE*
ADIPIC ACID
NYLON SALT
PLASTIC
FIBER
ADIPONITRILE
HEXAMETHYLENEDIAMINE
NYLON SALT
ADIPIC ACID ESTER
PLASTICIZERS
CYCLOHEXANOXIME
CAPROLACTAM
FIBER (PERLON)
CYCLOHEXANONE

DODECYL BENZENE

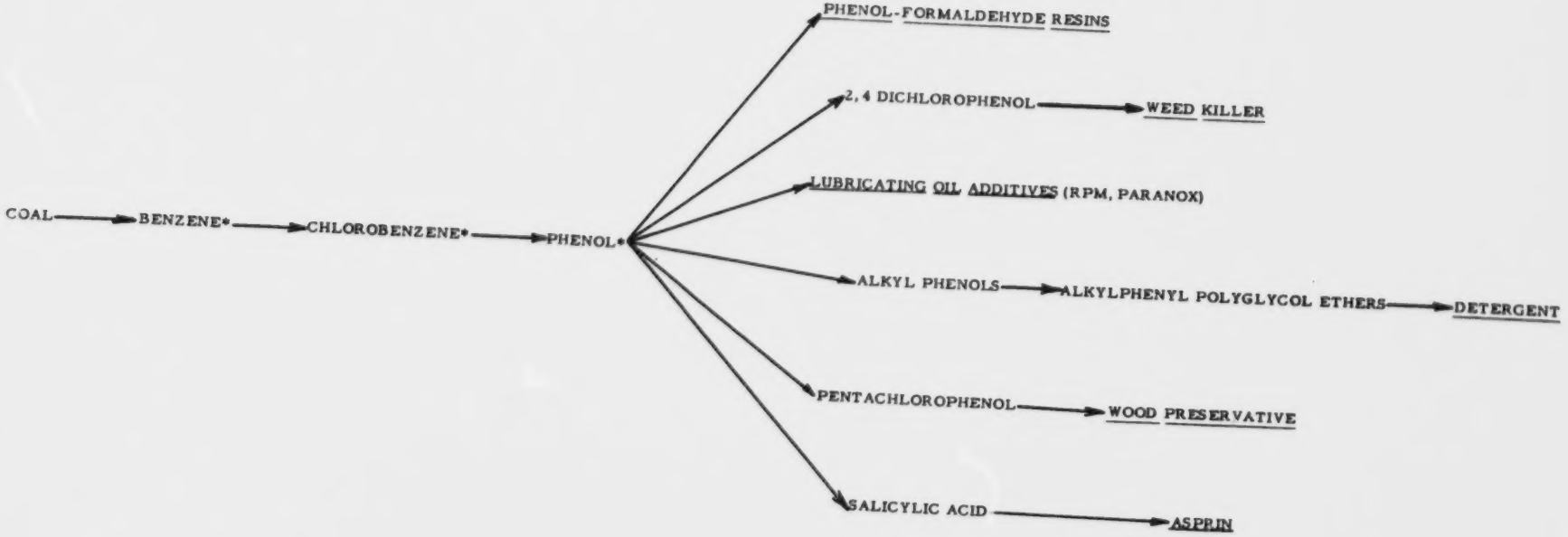
PETROLEUM → PROPYLENE* → PROPLYENE TETRAMER → DODECYL BENZENE * → DODECYL BENZENE SULFONATE → DETERGENT

ETHYL BENZENE

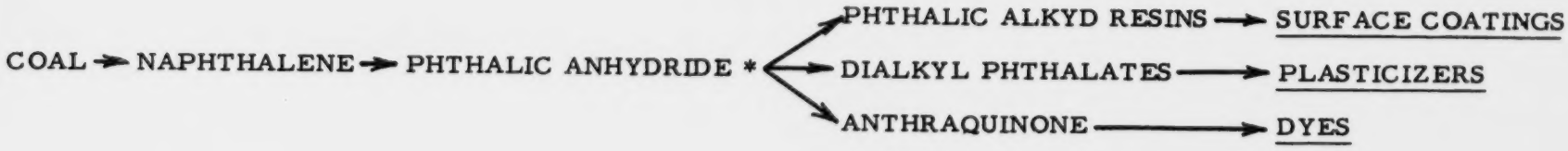



ETHYLENE
PETROLEUM
ETHYLENE
ETHYL ALCOHOL
SOLVENT
ETHYL ETHER
SOLVENT
ACETALDEHYDE
ACETIC ACID
ACETIC ANHYDRIDE
ACETYLSALICYLIC ACID
ASPRIN
ACETANILIDE
SULFA DRUGS
ETHYL ACETATE
SOLVENT
ETHYL ACETOACETATE
VITAMIN B1
BUTYL ACETATE
SOLVENT
ISOPROPYL ACETATE
SOLVENT
CHLOROACETIC ACID
2,4 DICHLOROPHYNOXYACETIC ACID
WEED KILLER
INDIGOID DYES
CYANOACETIC ACID
ORGANIC SYNTHESIS
ALDOL
n-BUTYL ALCOHOL
n-BUTYL ACETATE
SOLVENT
n-BUTRALDEHYDE
BUTYRALDOL
PLASTICIZER
n-BUTYRIC ACID
n-BUTYRIC ANHYDRIDE
CHLORAL
D.D.T.
INSECTIDE
PARALDEHYDE
METHYL ETHYL PYRIDINE
METHYL VINYL PYRIDINE
SYNTHETIC FIBER
NICOTINIC ACID
NICOTINAMIDE
VITAMIN
VITAMIN
PYRIDINE
FABRIC WATERPROOFING (ZELAN)
ANTIHISTAMINES
MEDICINALS
ETHYLENE OXIDE
ETHYLENE GLYCOL
ANTIFREEZE (PRESTONE)
ETHYLENE GLYCOL DINITRATE
INDUSTRIAL EXPLOSIVE
POLYESTER RESINS
DIETHYLENE GLYCOL
HUMECTANT
POLYETHYLENE GLYCOL
EMULSIFIERS
ETHYLENE CYANHYDRIN
ACRYLONITRILE
POLYACRYLONITRILE
FIBERS (ORLON)
SOIL CONDITIONERS
GR-A RUBBER
GLYCOL ETHERS
SOLVENT
ALKYLPHENYL POLYGLYCOL ETHERS
DETERGENTS
ETHANOLAMINES
TRIETHANOLAMINE LAURYL SULFATE
DETERGENTS
EMULSIFIERS (LIQUID WAXES)
ACID ABSORBENT
THIODIGYLCOL
MUSTARD GAS
ETHYL CHLORIDE
TETRAETHYL LEAD
ETHYL FLUID (GASOLINE ANTI-KNOCK ADDITIVE)
ETHYLENE DICHLORIDE
VINYL CHLORIDE
POLYVINYL CHLORIDE AND COPOLYMERS (VINYLITE, TYGON)
SOLVENT
TRICHLOROETHYLENE
VINYLIDENE CHLORIDE
POLYVINYLIDENE CHLORIDE (SARAN)
POLYETHYLENE
PLASTIC

PHENOL


COAL
BENZENE*
CHLOROBENZENE*
PHENOL*
PHENOL-FORMALDEHYDE RESINS
2, 4 DICHLOROPHENOL
WEED KILLER
LUBRICATING OIL ADDITIVES (RPM, PARANOX)
ALKYL PHENOLS
ALKYLPHENYL POLYGLYCOL ETHERS
DETERGENT
PENTACHLOROPHENOL
WOOD PRESERVATIVE
SALICYLIC ACID
ASPRIN

PHTHALIC ANHYDRIDE



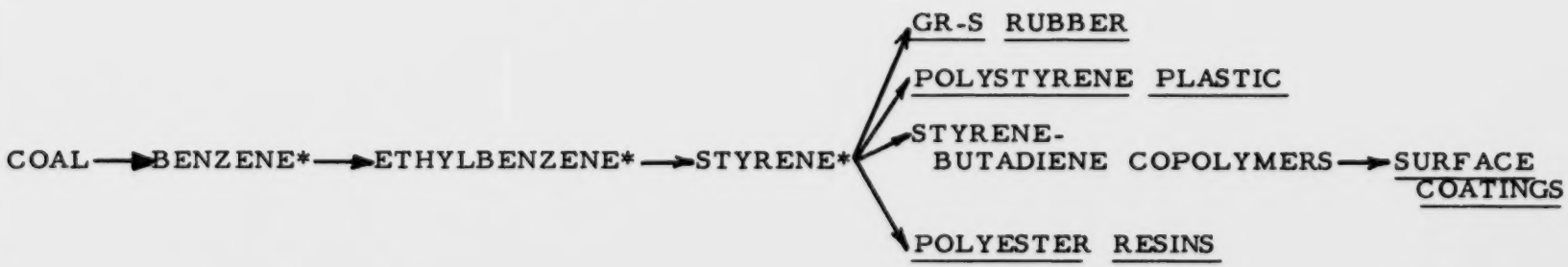
PROPANE

NATURAL GAS ——→ PROPANE *

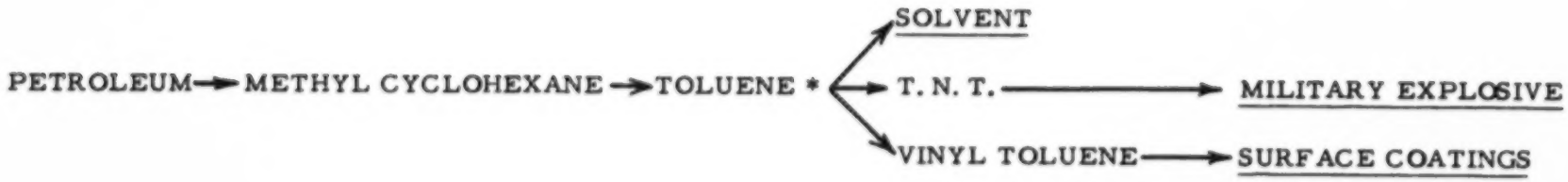
PROPYLENE

PETROLEUM
PROPYLENE*
ISOPROPYL ALCOHOL
ACETONE
DIACETONE ALCOHOL
METHYISOBUTYL KETONE
SOLVENT
METHYISOBUTYL CARBINOL
SOLVENT
SOLVENT
KETENE
ACETONE CYANHYDRIN
METHYL METHACRYLATE
POLYMETHYL METHACRYLATE
LUCITE
SOLVENT
ISOPROPYL ACETATE
SOLVENT
PROPYLENE TETRAMER
DODECYL BENZENE*
DODECYL BENZENE SULFONATE
DETERGENTS
PROPYLENE CHLOROHYDRIN
PROPYLENE OXIDE
PROPYLENE GLYCOL
SOLVENT
HYDRAULIC FLUID
ANTIFREEZE
ALLYL CHLORIDE
GLYCERINE DICHLOROHYDRIN
EPICHLOROHYDRIN
RESINS
ISOBUTYRALDEHYDE
ISOBUTYL ALCOHOL

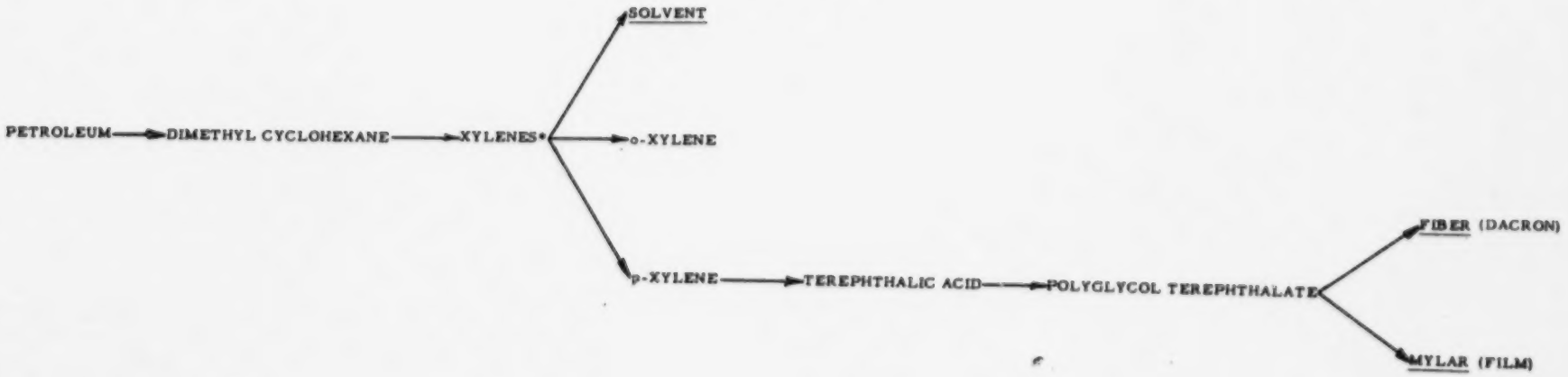
STYRENE


COAL
BENZENE*
ETHYLBENZENE*
STYRENE*
GR-S RUBBER
POLYSTYRENE PLASTIC
STYRENE-
BUTADIENE COPOLYMERS
SURFACE
COATINGS
POLYESTER RESINS

TOLUENE


PETROLEUM
METHYL CYCLOHEXANE
TOLUENE *
SOLVENT
T. N. T.
MILITARY EXPLOSIVE
VINYL TOLUENE
SURFACE COATINGS

XYLENE


PETROLEUM
DIMETHYL CYCLOHEXANE
XYLENES*
SOLVENT
o-XYLENE
p-XYLENE
TEREPHTHALIC ACID
POLYGLYCOL TEREPHTHALATE
FIBER (DACRON)
MYLAR (FILM)

END PRODUCTS SELECTED FOR STUDY

From data contained in the Stanford Research Institute "Chemical Economics Handbook", Volume V, End Chemical Groups, the following end products have been chosen for study.

End Product	Number of Times Mentioned on Previous Charts	1950 Dollar Value of Production in Millions of Dollars
Solvents	18	205
Medicinals	8	420
Fibers	6	1,173
Plastic	5	946 (with resins)
Rubber	5	284
Resins	4	946 (with plastics)
Surface Coatings	4	-
Synthetic Detergents	4	153 (surfactants)
Dyes	3	204
Explosives	3	140 (with propellants)
Insecticides	3	75
Plasticizers	3	-
Antifreezes	2	60
Gas and Oil Additives	2	252
Weed Killers	2	-
Total		3,912

The fifteen end products noted above represent 71.1 per cent of the total listed dollar value of end products produced in 1950. Eighty total end products were noted with fifty-five minor ones accounting for only 450 million dollars value production.

PRODUCTION OF END PRODUCTS AND PROBABLE CONSTITUENTS OF WASTE STREAMS

Since these charts were prepared from the ones presented in the previous section, the same criteria apply as were listed there. Three points must be emphasized to avoid misinterpretation. They are as follows:

1. An end product manufactured from several intermediates will only be listed as having one immediate predecessor which in turn will have all of its predecessors. In reality the product should have all of its immediate predecessors listed and each of these several immediate predecessors should have all of their predecessors listed. If this were the case all of the possible constituents in the waste stream from the manufacture of that product would be listed. Since this is not the case, this list must be viewed as somewhat incomplete, but of manageable length.

2. Sometimes the change from one intermediate to another is merely by direct oxidation, but often the change is brought about by the reaction with other chemicals. In these latter cases the reacting chemicals would also be possible constituents of the waste streams from the production process involved. These chemicals are not included in the listings, again making the list somewhat incomplete. Limitations of space and time preclude getting a complete tabulation.

3. The manufacture of a final commercial product from the last chemical in the list often is merely a case of adding other substances, e. g. the manufacture of commercial synthetic detergents from alkyl benzene sulfonate is often just the addition of phosphate builders. In other cases a definite chemical reaction is involved; e. g. the production of T. N. T. from toluene. Except for the solvents

and where definite trade names are given, generalized names have been listed for the final end product. Whether the production of the final commercial end product would contribute to the waste problem is not known. This would depend on the use of wet or dry processes of manufacture or blending, and would vary with each plant or process.

Possible Constituents of Waste Streams

Basic Raw Material	Intermediates	End Product
	SOLVENTS	
Benzene	Chlorobenzene	o-Dichlorobenzene
Petroleum	Dimethyl Cyclohexane	Xylene
Ethylene	Ethyl Alcohol, Acetaldehyde, Acetic Acid	Ethyl Acetate
Ethylene	Ethyl Alcohol, Acetaldehyde, Acetic Acid	Butyl Acetate
Ethylene	Ethyl Alcohol, Acetaldehyde, Acetic Acid	Isopropyl Acetate
Ethylene	Ethyl Alcohol, Acetaldehyde, Adol, n-Butyl Alcohol	n-Butyl Acetate
Ethylene	Ethyl Alcohol, Acetaldehyde, Adol	n-Butyl Alcohol
Ethylene	Ethylene Chlorohydrin, Ethylene Oxide	Glycol Ether
Ethylene		Ethylene Dichloride
Ethylene		Ethyl Alcohol
Ethylene	Ethyl Alcohol	Ethyl Ether
Propylene	Isopropyl Alcohol, Acetone, Diacetone Alcohol	Methyl Isobutyl Keytone
Propylene	Isopropyl Alcohol, Acetone, Diacetone Alcohol, Methyl Isobutyl Ketone	Methyl Isobutyl Carbinol
Propylene	Isopropyl Alcohol	Acetone
Propylene		Isopropyl Alcohol
Propylene	Isopropyl Alcohol	Isopropyl Acetate
Propylene	Propylene Chlorohydrin, Propylene Oxide	Propylene Glycol
Petroleum	Methyl Cyclohexane	Toluene

Possible Constituents of Waste Streams

Basic Raw Material	Intermediates	End Product
	MEDICINALS	
Benzene	Chlorobenzene, Phenol, Salicylic Acid	Aspirin
Benzene	Nitrobenzene, Aniline, Acetanilide	Sulfa Drug
Ethylene	Ethyl Alcohol, Acetaldehyde, Acetic Acid, Acetic Anhydride, Acetylsalicylic Acid	Aspirin
Ethylene	Ethyl Alcohol, Acetaldehyde, Acetic Acid, Acetic Anhydride, Acetanilide	Sulfa Drug
Ethylene	Ethyl Alcohol, Acetaldehyde, Acetic Acid, Ethyl Acetate, Ethylacetoacetate	Vitamin B_1
Ethylene	Ethyl Alcohol, Acetaldehyde, Paraldehyde, Methyl Ethyl Pyridine, Nitotinic Acid, Nicotiamide	Vitamin
Ethylene	Ethyl Alcohol, Acetaldehyde, Paraldehyde, Methyl Ethyl Pyridine, Nicotinic Acid	Vitamin
Ethylene	Ethyl Alcohol, Acetaldehyde, Paraldehyde, Pyridine	Antihistimines
	FIBERS	
Benzene	Cyclohexane, Adipic Acid, Nylon Salt	Nylon
Benzene	Cyclohexane, Adipic Acid, Adiponitrile, Hexamethylenediamene, Nylon Salt	Nylon
Benzene	Cyclohexane, Adipic Acid, Cyclohexanoxime, Caprolactam	Perlon
Petroleum	Dimethylcyclohexane, p-Xylene, Terephthalic Acid, Polyglycol Terephthalate	Dacron

Possible Constituents of Waste Streams

Basic Raw Material	Intermediates	End Product
	FIBERS (Cont.)	
Ethylene	Ethyl Alcohol, Acetaldehyde, Paraldehyde, Methyl Ethyl Pyridine, Methyl Vinyl Pyridine	Synthetic Fiber
Ethylene	Ethylene Chlorohydrin, Ethylene Oxide, Ethylene Cyanhydrin, Acrylonitrile, Polyacroylonitrile	Orlon
	PLASTICS	
Benzene	Ethylbenzene, Styrene, Polystyrene	Plastic
Benzene	Cyclohexane, Adipic Acid, Nylon Salt	Plastic
Ethylene	Polyethylene	Plastic
Ethylene	Ethylene Dichloride, Vinyl Chloride, Polyvinylchloride	Tygon
Propylene	Isopropylalcohol, Acetone, Acetone Cyanhydrin, Methyl Methacrylate, Polymethyl Methacrylate	Lucite
	RUBBERS	
Benzene	Ethylbenzene, Styrene	GR-S Rubber
Benzene	Nitrobenzene, Aniline	Rubber Processing Chemicals
Ethylene	Ethylene Chlorohydrin, Ethylene Oxide, Ethylene Cyanhydrin, Acrylonitrile	GR-A Rubber
n-Butylene	Butadiene	GR-S Rubber
n-Butylene	Butadiene	GR-A Rubber
	RESINS	
Benzene	Ethylbenzene, Styrene	Polyester Resin
Benzene	Chlorobenzene, Phenol	Phenol-Formaldehyde Resin
Ethylene	Ethylene Chlorohydrin, Ethylene Oxide, Ethylene Glycol	Polyester Resin

Possible Constituents of Waste Streams

Basic Raw Material	Intermediates	End Product
	RESINS (Cont.)	
Propylene	Allyl Chloride, Glycerine Dichlorohydrin, Epichlorohydrin	Resin
	SURFACE COATINGS	
Benzene	Ethylbenzene, Styrene, Styrene-Butadiene Copolymers	Surface Coating
Petroleum	Methyl Cyclohexane, Toluene, Vinyl Toluene	Surface Coating
n-Butylene	Butadiene, Styrene-Butadiene Copolymers	Surface Coating
Naphthalene	Phthalic Anhydride, Phthalic Alkyd Resin	Surface Coating
	SYNTHETIC DETERGENTS	
Benzene	Chlorobenzene, Phenol, Alkyl Phenol	Synthetic Detergent
Ethylene	Ethylene Chlorohydrin, Ethylene Oxide, Alkyl Phenylpolyglycol Ethers	Synthetic Detergent
Propylene	Propylene Tetramer, Dodecylbenzene, Dodecylbenzene Sulfonate	Synthetic Detergent
Ethylene	Ethylene Chlorohydrin, Ethylene Oxide, Ethanolamine, Triethanolamine Lauryl Sulfate	Synthetic Detergent
	DYES	
Benzene	Nitrobenzene, Aniline	Dye
Ethylene	Ethyl Alcohol, Acetaldehyde, Acetic Acid, Chloroacetic Acid, Indigoid	Dye
Naphthalene	Phthalic Anhydride, Anthraquinone	Dye

Possible Constituents of Waste Streams

Basic Raw Material	Intermediates	End Product
	EXPLOSIVES	
Benzene	Nitrobenzene, Aniline, Dimethyl Aniline	Tetryl
Petroleum	Methyl Cyclohexane, Toluene	T. N. T.
Ethylene	Ethylene Chlorohydrin, Ethylene Oxide, Ethylene Glycol, Ethylene Glycol Dinitrate	Explosive
	INSECTICIDES	
Benzene	Chlorobenzene	D. D. T.
Benzene	Chlorobenzene, p-Dichlorobenzene	Insecticide
Ethylene	Ethyl Alcohol, Acetaldehyde, Chloral	D. D. T.
	PLASTICIZERS	
Benzene	Cyclohexane, Adipic Acid, Adipic Acid Esters	Plasticizer
Ethylene	Ethyl Alcohol, Acetaldehyde, Aldol, n-Butraldehyde	Plasticizer
Naphthalene	Phthalic Anydride, Dialkyl Phthalate	Plasticizer
	ANTIFREEZES	
Ethylene	Ethylene Chlorohydrin, Ethylene Oxide, Ethylene Glycol	Prestone
Propylene	Propylene Chlorohydrin, Propylene Oxide, Propylene Glycol	Antifreeze
	GAS AND OIL ADDITIVES	
Benzene	Chlorobenzene, Phenol	Lubricating Oil Additives
Ethylene	Ethyl Chloride, Tetraethyl Lead, Ethyl Fluid	Anti-Knock Additive

Possible Constituents of Waste Streams

Basic Raw Material	Intermediates	End Product
	WEED KILLERS	
Benzene	Chlorobenzene, Phenol, 2,4 Dichlorophenol	Weed Killer
Ethylene	Ethyl Alcohol, Acetaldehyde, Acetic Acid, Chloroacetic Acid, 2,4 Dichloro-phenoxyacetic Acid	Weed Killer

Note: Due to the fact that few manufacturing processes are 100 per cent recovery processes, some of the manufactured end product will probably be found in waste streams.

MANUFACTURING PROCESSES FOR END PRODUCTS

From the text by R. N. Shreve on "Selected Process Industries" and the text by W. L. Faith, D. B. Keyes and R. L. Clark on "Industrial Chemicals", the following manufacturing processes have been listed.

SOLVENTS

o-Dichlorobenzene - By product from the manufacture of monochlorobenzene.

Xylene - Naphtha is added to a furnace, heated, passed to a reactor and then to a gas separator. From the gas separator the material is run through a stabilizing column from which the hydroformate is passed through a primary toluene column. There, in addition to toluene, the xylene is drawn off.

Ethyl Acetate - Ethyl alcohol in excess and acetic acid are passed through an esterification column. Ethyl acetate is continuously removed.

Butyl Acetate - Similar to ethyl acetate except butyl alcohol is used.

Isopropyl Acetate - No listing.

n-Butyl Acetate - Acetic acid and n-butyl alcohol (10 per cent excess) are mixed in batch still with 0.1 per cent sulfuric acid as a catalyst. At constant temperature the distillate is rapidly removed.

n-Butyl Alcohol - No listing.

Glycol Ether - Absolute ethyl alcohol (15 per cent excess) and liquid ethylene oxide are mixed under pressure in an autoclave at 150°C for twelve hours. Cellosolve (ethylene glycol ethyl ether) is taken off at 134°C.

Ethylene Dichloride - Chlorine gas is bubbled through a tank of ethylene dibromide and then mixed with ethylene in a chlorinating

tower. The mixture is then taken to a partial condenser and a separator.

Ethyl Alcohol - Ethylene is absorbed in sulfuric acid to give a mixture of ethyl sulfates which are then hydrolyzed to crude ethyl alcohol and dilute sulfuric acid. The alcohol is purified by distillation and the acid is concentrated for reuse.

Ethyl Ether - Ethyl alcohol and sulfuric acid are heated and the vapors scrubbed by a sodium hydroxide solution and taken to a fractionating column. Water is drawn from the bottom of the tower to waste, ethyl ether is taken from the top and ethyl alcohol is removed at the middle of the tower.

Methyl Isobutyl Ketone - No listing.

Methyl Isobutyl Carbinol - No listing.

Acetone - Air and isopropyl alcohol are vaporized and passed through a reactor at 400 to 600°C, the hot gases are scrubbed and cooled with water, nitrogen being released to the atmosphere. The mixture goes to a column where acetone is removed at the top and water and isopropyl alcohol are taken off at the bottom for recovery.

Isopropyl Alcohol - Propylene is absorbed by sulfuric acid to form propyl sulfate which is then hydrolyzed with water to form isopropyl alcohol and dilute sulfuric acid.

Isopropyl Acetate - No listing.

Propylene Glycol - No listing.

Toluene - From fractions of petroleum which are rich in naphthlenes, dimethylcyclopentane, methylcyclohexane, and ethylcyclopentane are catalytically dehydrogenated in the presence of hydrogen to form a mixture of aromatic hydrocarbons, chiefly toluene.

MEDICINALS

Salicylic Acid - Phenol plus equimolar amounts of hot aqueous caustic soda are heated to 130°C, evaporated to dryness in stirred autoclaves under vacuum. After drying, the temperature is reduced to 100°C and carbon dioxide gas is blown into the reaction chamber at about 100 psi. Finally the charge is heated to 150 to 170°C for several hours.

None of the other medicinals listed.

FIBERS

Nylon - Adipic acid and hexamethylenediamene are heated under pressure to form nylon salt which is shipped in solution to the fiber manufacturing plant. None of the other fibers listed.

PLASTICS

None listed.

RUBBERS

GR-S Rubber - Styrene, butadiene, soap solution, water, initiating catalyst and a chain modifying agent are autoclaved at 52°C for 15 to 20 hours and then taken for further processing. Excess butadiene and styrene are recovered, the latex flucculated with a little alkali and some glue. The soap is converted to fatty acids with dilute sulfuric acid.

Other rubbers not listed.

RESINS

Phenol-Formaldehyde Resins (Cast Type) - Phenol, formaldehyde and a catalyst (barium hydroxide or caustic soda) are heated at 160°F for 10 to 30 minutes. Then 75 per cent of the water is removed under vacuum and an organic acid (lactic, phthalic anhydride

or maleic) is added to neutralize the caustic and clarify the color. Before the final dehydration, platicizers, pigments and colors are added and mixed. Final dehydration is effected under vacuum and the resins hardened in preheated moulds at 185°F for five days.

Other resins not listed.

SURFACE COATINGS

None listed.

SYNTHETIC DETERGENTS

None listed.

DYES

None listed.

EXPLOSIVES

Tetryl - Sulfuric acid and nitric acid are mixed with dimethylaniline.

T. N. T. - Toluene is nitrated with mixed acids in cast iron nitrators.

Other explosives not listed.

INSECTICIDES

D. D. T. - Chloral, chlorobenzene and concentrated sulfuric acid are mixed at 15 to 30°C for five to six hours. Sedimentation removes the excess acid. After neutralization with sodium carbonate the material is run to a column where it is vacuum distilled and then air distilled to eliminate the chlorobenzene.

Other insecticides not listed.

PLASTICIZERS

None listed.

ANTIFREEZES

None listed.

GAS AND OIL ADDITIVES

None listed.

WEED KILLERS

None listed.

SUMMARY AND RECOMMENDATIONS

The industrial waste problem in the United States today is a vast and complex one. In addition to the organic chemical industry, many other areas of pollution potential exist. Food processing, petroleum refining, dairy, paper and pulp, and inorganic waste sources must be recognized and dealt with if the water resources of the country are to be maintained in their present condition or improved. Some of the problems are old ones; some have been throughly studied and solved; but some are new. It is these new problems which must receive immediate attention, particularly if their magnitude is great and their scope is national. One such new problem is the rapidly developing petrochemical industry, that is, the production of organic chemicals from petroleum and natural gas, and the closely allied field of chemical production from coal.

These industries present problems from two points of view; 1) their production is widely varied so their waste streams are complex; and 2) their production is increasing at a phenomenal rate. The first point of view makes the waste problem difficult to investigate; the second makes it imperative that the waste problem be investigated.

In an effort to simplify the problem a search of the literature was made to find the major basic raw materials produced from petroleum, natural gas, and coal. The primary end products from these major chemicals were then listed with the probable constituents in the waste streams from the production of these end products. Study of treatability of the waste streams from plants which produce these end products would cover the major portion of the waste problems from the petrochemical and related industries. The companies which

produce the major raw materials were listed along with the location of their plants to allow easy consultation with the organizations which are in the business of supplying the raw materials upon which these petrochemical and related industries depend.

It is recommended that a program of research focus its attention first on the ability of known methods of waste treatment to handle the crude materials and key intermediates selected. Modifications of treatment operations will undoubtedly come from the research program, and new processes may be called for in order to achieve the necessary degree of treatment within the realm of economic reality. Such a research program can best be established through the counsel of an advisory board of chemical engineers, chemists, biologists and sanitary engineers familiar with the organic chemical industry and with the need for research in the petrochemical area. It has one of the highest pollution potentials of the water resources of the nation and warrants immediate study on the part of the Robert A. Taft Sanitary Engineering Center.